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REMOVAL OF HYDROGEN FROM CADMIUM PLATED HIGH STRENGTH STEEL BY BAKING - A STATISTICALLY DESIGNED STUDY

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Statistically designed screening experiments were conducted to determine the significance of various parameters on the hydrogen content of bright and dull cadmium plated 4340 steel after baking. It was shown that the baking time was essentially the only significant variable in determining the final hydrogen concentration as determined by the barnacle electrode. However, variations between batches were found to be significant for the dull cadmium plated material.

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A delay in baking of 24 hours had no effect on the final hydrogen content. Also, the hydrogen concentration was not altered if the specimens were held for a month at relative humidities of up to 50% after baking.

It was found that the barnacle electrode measurements decreased exponentially with the baking time, and that at least 100 hours were needed to bake out all of the hydrogen from parts plated with 0.015 mm of bright cadmium and 40 hours with dull cadmium.

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INTRODUCTION

Electrodeposited cadmium is widely used to protect low alloy, high strength steels from corrosion. It is generally recognized however that hydrogen produced during this plating can lead to catastrophic failure of a stressed structural part, such as aircraft landing gear (reference (a)). Because of this, plated parts must be baked to lower the hydrogen concentration and thus reduce the possibility of failure. The conventional bright cadmium plate deposited from cyanide baths is preferred due to its appearance and protective characteristics. However, this coating is a barrier toward hydrogen diffusion; even prolonged baking might not necessarily drive off all of the hydrogen (references (b) and (c)). The problem of hydrogen embrittlement becomes more severe with increased strength. Thus AISI 4340 steel at a strength level of 1790-1930 MPa (260-280 ksi) with an acute notch (K_t=5.6) might be embrittled with less than 0.1 ppm mobile hydrogen (reference (c)). Therefore, low embrittlement baths are used for high strength steels. These produce duller and more porous plates which lose hydrogen more readily upon baking. The dull cadmium is not as protective as the bright however.

Specifications for baking cadmium plated, high strength steels to relieve hydrogen embrittlement tend to be rather vague, such as, "bake for 1-5 hours at 150-205 C (300-400 F)" (reference (d)). In the aircraft industry, as at this laboratory, it is common practice to bake for 24 hours at 190 C (375 F) for the highest strength steels, and/or to use a sliding scale depending on the strength level.

It is also common practice to bake "as soon as possible after plating" (reference (d)). This is done to prevent hydrogen damage in case the parts have not been stress relieved. However, whether this alters the final hydrogen concentration, as has been reported (reference (e)), is questionable.

Traditionally, mechanical testing has been the only way to determine the effectiveness of the bakeout. Measurement of total hydrogen has also been used, but it is questionable if there is any correlation between total hydrogen and embrittlement. Since the development of the barnacle electrode, (references (c) and (f)), it is possible to measure mobile, or embrittling, hydrogen and thus determine optimum baking conditions. Correlations with mechanical testing are, of course, still necessary.

In a previous study (reference (c)), it was shown that a correlation between mobile hydrogen and sustained load failure could be established. As this work was done with unplated material, data must still be established with plated material. Before this can be done, however, several parameters had to be investigated to determine their effects on the mobile hydrogen. These include: the time between plating and baking and the time between baking and measuring the hydrogen to establish whether or not the hydrogen concentration is constant over a long period as there will be a wide range of times-to-failure in sustained load testing.

This study was therefore undertaken to elucidate the effects of some of the variables associated with the post cadmium plating bakeout of high strength steels.

so that a more effective bakeout might be achieved, preliminary to correlations with mechanical testing.

A statistically designed approach was used to screen the variables and obtain the most information (reference (g)). Five varabiles were investigated, using two levels for each. The variables were: two plating batches, a delay between plating and baking, a delay between baking and measuring, the humidity conditions during this latter delay, and the baking time. Using a Plackett-Burman design, these five variables were analyzed using 12 specimens. A complete two-level design in five variables would require at least 64 specimens. The design used here offers a very good statistical treatment of the experimental error and a measure of the significance of the individual variables between the limits chosen.

This study was conducted as part of an ongoing research program on corrosion and hydrogen embrittlement, AIRTASK NO. WR02201001, WORK UNIT NO. DG202.

E X P E R I M E N T A L P R O C E D U R E S

The specimens were approximately 40 mm (1.5 in) square, 1 mm (0.04 in) thick pieces of AISI 4340 steel heat treated to 1790-1930 MPa (260-280 ksi) strength level. They were plated with 0.015 mm (0.0005 in) of bright or dull cadmium using a conventional cyanide bath, with or without brighteners. Plating conditions are given in Appendix A. The specimens were baked at 190 C (375 F). The cadmium was removed, for hydrogen measurements, by swabbing with ammonium nitrate solution (120 g/L; 1 lb/gal). The barnacle electrode, which is described elsewhere (reference (c)), was used for these measurements. In this method, the electrochemical current due to oxidation of the extracted hydrogen is measured. The current at any given time, such as at 30 minutes, can be related to the mobile hydrogen concentration of the specimen. The 30 minute barnacle electrode measurements ($\mu A/cm^2$) were used to indicate the relative hydrogen levels. No attempt was made to calculate actual hydrogen concentrations (reference (c)).

The mean, ambient relative humidity for the bright cadmium screening experiment was 35%. The 50% relative humidity for the dull cadmium experiment was obtained over a saturated solution of sodium dichromate.

The 12-run Plackett-Burman design (reference (g)) used to screen the five variables is shown in Table I. The pluses and minuses in Table I indicate limits of conditions, such as high/low, yes/no, etc. The variables chosen and their limits for the bright and dull cadmium experiments are given in Table II. The specimens were randomized in the plating rack, including extra ones in order to have a full rack in each batch. The five variables were arbitrarily assigned to columns X_1-X_5; the unassigned columns (X_6-X_{11}) (cf. Table I), were used to calculate the experimental error.

The design for the two-variable experiment, along with the variable limits and center points is shown in Table III.

TABLE I

TWELVE-RUN PLACKETT-BURMAN DESIGN

Trial	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	X_{10}	X_{11}
1	+	+	−	+	+	+	−	−	−	+	−
2	+	−	+	+	+	−	−	−	+	−	+
3	−	+	+	+	−	−	−	+	−	+	+
4	+	+	+	−	−	−	+	−	+	+	−
5	+	+	−	−	−	+	−	+	+	−	+
6	+	−	−	−	+	−	+	+	−	+	+
7	−	−	−	+	−	+	+	−	+	+	+
8	−	−	+	−	+	+	−	+	+	+	−
9	−	+	−	+	+	−	+	+	+	−	−
10	+	−	+	+	−	+	+	+	−	−	−
11	−	+	+	−	+	+	+	−	−	−	+
12	−	−	−	−	−	−	−	−	−	−	−

Note: X_1, X_2, X_3 ... are variables.

TABLE II

VARIABLE LIMITS FOR BRIGHT AND DULL CADMIUM PLACKETT-BURMAN EXPERIMENTS

Column*	Variable	Limits			
		Bright		Dull	
		−	+	−	+
X_1	Plating batch	2	1	1	2
X_2	Time between plating and baking (h)	1	24	1	24
X_3	Baking time (h)	8	48	8	20
X_4	Time between baking and measuring (h)	2	690	2	690
X_5	Relative humidity (%)**	0	35	0	50

*Column corresponds to Table I.
**0%=desiccator; 35%=ambient; 50%=over saturated $Na_2Cr_2O_7$.

TABLE III

TWO-VARIABLE, TWO-LEVEL EXPERIMENTAL DESIGN
AND VARIABLE LIMITS, INCLUDING CENTER POINTS (CP)

Trial	Delay Time, h X_1	Bake Time, h X_2
1	1/4 (-)	3 (-)
2	24 (+)	3 (-)
3	1/4 (-)	72 (+)
4	24 (+)	72 (+)
CP	12 1/8	37½

D I S C U S S I O N O F R E S U L T S

A 12-run Plackett-Burman experiment was run with the conventional bright cadmium plated 4340 steel, and another with a low embrittlement (dull) cadmium. In this experimental design, the variables can be assigned to any columns. The unassigned columns are then used to determine the experimental error. When assigning a factor (variable) to a column, the high and low limits (or batch number, etc.) for this factor only are automatically chosen by the "+" or "-". There is a random distribution for the unassigned columns. Thus by comparing the results of the barnacle electrode measurements for all of the specimens in which a particular variable is at its high value to those in which it is low, one can determine whether or not that factor affects the results. Inherent in the design is a replication, making duplicate runs unnecessary.

The 30-minute barnacle electrode measurements (showing the relative, residual mobile hydrogen after baking) are given in Table IV. For comparison, specimens allowed to outgas in a desiccator give background readings of 0.22 $\mu A/cm^2$ for these specimens. In order to determine the factor effect, the average measurements for the high values are compared to those for the low. For example, the longer baking times (+) were for trials 2, 3, 4, 8, 10 and 11 (see Table IV). The sum of the barnacle electrode readings for these six specimens in the bright cadmium experiment is 3.26. Similarly, the sum for the shorter baking time is 5.36. Taking the difference and dividing by the number of pluses gives the factor effect, 0.35 in this example.

The minimum significant factor effect, [MIN], is calculated using the unassigned columns. First, the unassigned factor effect, UFE, for each column is calculated in the same way as above. This is then used to determine the significant factor effect, S_{FE}, which is an estimate of the experimental error,

$$S_{FE} = \sqrt{\frac{\sum_{i=1}^{q} UFE_i^2}{q}}$$

where q is the number of degrees of freedom (the number of unassigned columns). Then

$$[MIN] = t \cdot S_{FE}$$

where t is obtained from the t-distribution table using q=6. [MIN] is given in Table V for both the 90 and 95% confidence levels. With six degrees of freedom, the 95% level is justified.

TABLE IV

BARNACLE ELECTRODE MEASRUEMENTS AND SAMPLE CALCULATION FOR PLACKETT-BURMAN SCREENING EXPERIMENTS

Trial	Bake, X_3	Barnacle Reading, $\mu A/cm^2$	
		Bright Cadmium	Dull Cadmium
1		1.15	0.68
2	−	.34	.27
3	+	.74	.30
4	+	.54	.50
5	−	.97	.56
6	−	.97	.65
7	−	.78	.42
8	+	.33	.34
9	−	.58	.36
10	+	.60	.36
11	+	.71	.30
12	−	.91	.43
Sum +		3.26	2 07
Sum −		5.36	3.10
Difference		2.10	1.03
Factor Effect (÷6)		0.35	0.17

To determine the importance of the variables, their factor effects must be compared to the [MIN]. If the absolute value of the factor effect is larger than the [MIN], then the variable is statistically significant. From Table V, one can see that for the bright cadmium, only the baking time is significant whereas with the dull cadmium, the batch is also significant. The reason for this is probably that small changes in concentrations of the bath ingredients, especially carbonate, can have a significant effect on the nature of the deposit from a dull cadmium bath. In this experiment, the two batches were plated one week apart.

TABLE V

FACTOR EFFECTS AND MINIMUM SIGNIFICANT FACTOR EFFECTS, [MIN], FOR THE BRIGHT AND DULL CADMIUM PLACKETT-BURMAN EXPERIMENTS

Variable	Factor Effect	
	Bright	Dull
X_1 Batch	0.087	0.145*
X_2 Delay before baking	.127	.038
X_3 Baking time	.350*	.172*
X_4 Delay after baking	.040	.065
X_5 Humidity	.077	.005
S_{FE} (experimental error)	.119	.048
MIN 95% confidence level, t=2.45	.291	.118
MIN 90% confidence level, t=1.94	.230	.093

*Significant factor effects

The factor effects for the two delays and the humidity were shown to be statistically insignificant. This means that any delay up to 24 hours before baking will have no effect on the mobile hydrogen concentration. These results do not, of course, preclude the possibility that materials under stress might be damaged if baking is delayed. The delay in measuring was found to be insignificant up to 690 hours (approximately one month) at moderate humidities. This means that delayed failure testing vs. mobile hydrogen measurements can be made with confidence that the hydrogen concentration will not change with time. It also means that interlaboratory, or other testing, involving delayed hydrogen measurements can be done with no need to coordinate the times for measurements. Also, specimens plated with cadmium do not have to be kept cold until measuring, as is common practice. Extremely long times, e.g. one year, at very high humidities, e.g. 90%, could alter these conclusions.

Because of the concern that the delay between plating and baking could be important, it was decided to run a check experiment using just two variables: delay before baking and baking time, with the bright cadmium plate. Low, high and center points were used with duplicates for each (reference (g)). This required ten specimens, or one batch. Broader limits than in the 12-run experiments were chosen. As can be seen from Table VI, the measurements for short or long baking times are in excellent agreement regardless of delay time; that is, trials 1 and 2 agree with each other, as do 3 and 4. The statistical calculations are therefore unnecessary.

TABLE VI

BARNACLE ELECTRODE MEASUREMENTS FOR THE TWO-VARIABLE BRIGHT CADMIUM EXPERIMENT

Trial*	Barnacle Measurements, $\mu A/cm^2$	Average
1	0.88 ; 1.26	1.07
2	1.08 ; 1.02	1.05
3	0.26 ; 0.31	.28
4	0.28 ; 0.31	.30
CP	0.55 ; 0.40	.48

*See Table III

The plots of the hydrogen currents vs. the log of the bakeout time from this last experiment and that from the dull cadmium experiment are shown in Figure 1. The lines represent the best fit of the measurements for the 10 and 12 points, respectively (Tables IV and VI). Extrapolations of the curves show that complete bakeout is obtained at times well beyond any normal procedures, 100 and 40 hours, respectively, for the bright and dull plates. The "no hydrogen" level is the barnacle electrode measurement obtained with plated and stripped specimens which were desiccated for a week or more. The very low concentrations of hydrogen measured for the longer bakeout times are much too small to be calculated quantitatively. They are, however, well under 0.1 ppm (reference (c)). Further work on correlation with mechanical testing is necessary to determine how much baking is actually necessary to lower the hydrogen concentration to a safe level. Also, these data are for 1 mm thick specimens which have a much larger surface to volume ratio than actual parts might have.

C O N C L U S I O N S

Statistically designed screening experiments were conducted to determine the significance of various parameters on the post-baking hydrogen content of bright and dull cadmium plated 4340 steel. It was shown that the baking time was essentially the only significant variable influencing the final hydrogen concentration as determined by the barnacle electrode. However, variations between batches were found to be significant for the dull cadmium plated material.

A delay in baking of 24 hours had no effect on the final hydrogen content. Also, the hydrogen concentration was not altered if the specimens were held for a month at relative humidities of up to 50% after baking.

It was found that the barnacle electrode measurements decreased exponentially

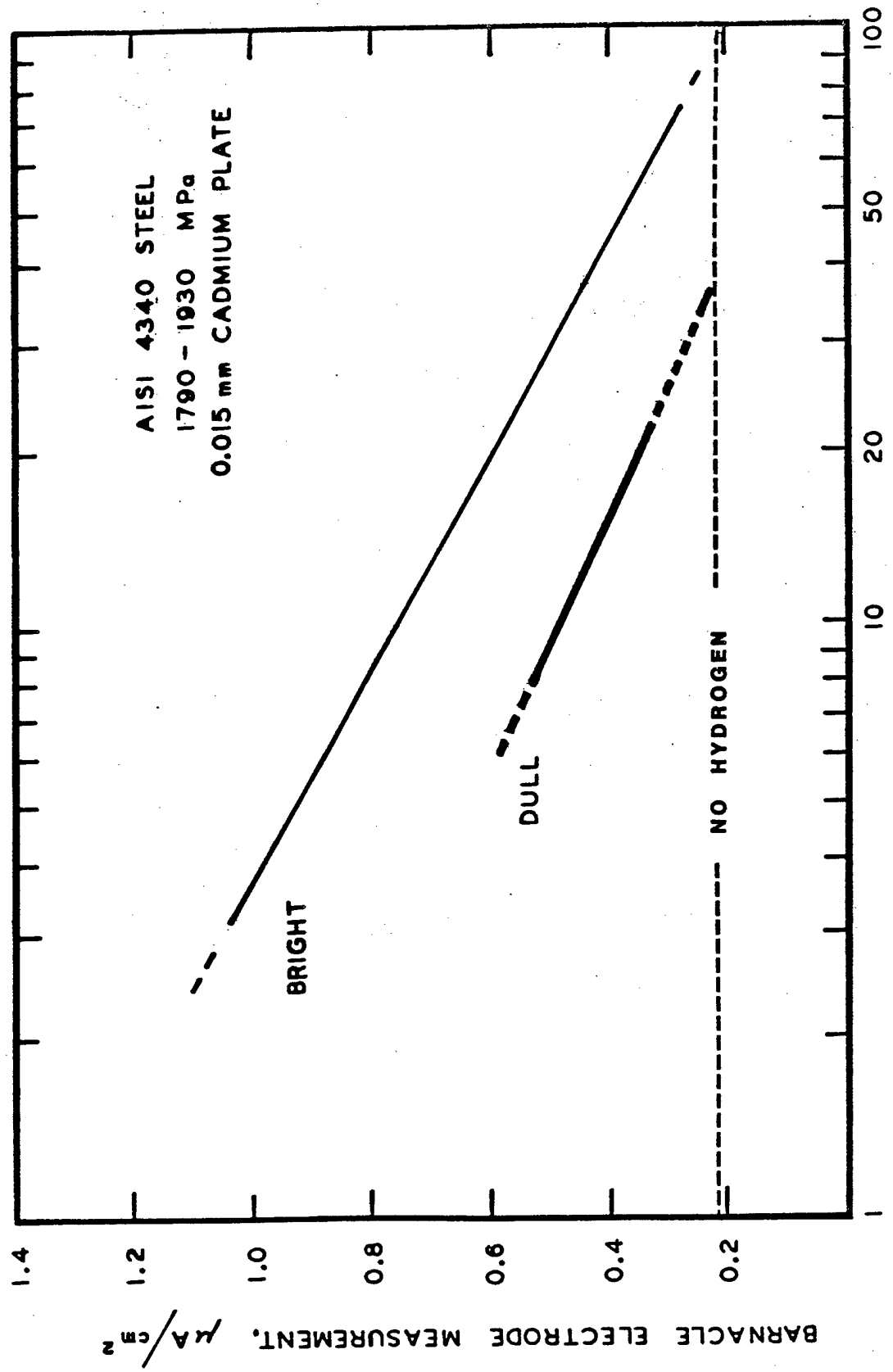

Figure 1. Efficiency of Baking Treatment for Removal of Hydrogen from Bright and Dull Cadmium Plated Steel.

with the baking time, and that at least 100 hours were needed to bake out all of the detectable hydrogen from parts plated with 0.015 mm of bright cadmium whereas 40 hours were required with dull cadmium.

FUTURE WORK

Work is continuting in the study of the embrittling effect of hydrogen in the cleaner steel, 300 M, in the area of correlation of hydrogen, sustained load and failure times of cadmium plated tensile specimens.

A C K N O W L E D G E M E N T S

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A P P E N D I X A

CADMIUM PLATING PARAMETERS

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CADMIUM PLATING PARAMETERS

	Bright	Dull
Sodium cyanide	16.0 oz/gal	13.6 oz/gal
Cadmium oxide	4.0 oz/gal	4.0 oz/gal
Udilite 53 brightener	1%	--
Sodium carbonate, adjust	--	2.0 oz/gal
Current density	25 A/ft^2	60 A/ft^2

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